THE HYDROLYSIS OF TERTIARY ARSENATES

BY

HAROLD BYRON JOHNS

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1922

UNIVERSITY OF ILLINOIS

May 29, 1922.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Harold Byron Johns

ENTITLED The Hydrolysis of Tertiary Arsenates

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering.

J. H. Reedy,
Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry

Digitized by the Internet Archive

in 2015

Table of Contents.

I.

Introduction.

(a). Facts suggesting the problem.

Lead arsenate has been used as an insecticide for several years. On account of the increased cost of manufacture, however, manufacturers have recently directed their attentions to the manufacture of a substitute, calcium arsenate, which can be produced for about one half the cost of the lead arsenate.

Calcium arsenate is now being manufactured in large quantities and is used in the south, principally for the destruction of the cotton boll worm and, to a lesser extent, for the tobacco worm, Colorado potato beetle, and the codling moth. It has been conclusively demonstrated that these two arsenates are equal in toxic value and killing power.

There is one great disadvantage in the use calcium arsenate as an insecticide in that, even though the product may be free from water soluble arsenic when it leaves the factory, it very often has an appreciable of water soluble arsenic when it reaches the consumer. This water soluble arsenic burns the foliage of plants and since it cannot be removed, large amounts of the insecticide are returned and cause a great loss to the manufacturer. Another disadvantage is that many batches are spoiled in preparation because of the difficulty of properly controlling the conditions of formation.

(b). Review of the literature.

Reedy and Haag (1) found that the presence of such impurities as NaCl or $FeSO_4$ seemed to catalyze the formation of water soluble As_2O_5. Exposure to air and carbon dioxide had similar effects.

De Toni (2) recently prepared colloidal tri-calcium phosphate by adding slowly and with constant stirring, nearly boiling N Na_3PO_4 solution, largely diluted, to an equal volume of hot N $CaCl_2$, which also had been largely diluted and had been mixed with the desired quantity of gelatin as protective colloid. He found that cold solutions react slowly and remain clear for a long time. By adding the phosphate to the calcium chloride an excess of Ca ions is assured and the formation of tri-calcium phosphate. Gelatin gives a precipitate with the sodium phosphate and is therefore added to the calcium chloride. De Toni prepared the Na_3PO_4 solution by adding the calculated amount of NaOH to a solution of Na_2HPO_4, diluting to normal and then carefully protecting from the air. By varying the concentrations he found that to make colloidal solutions containing 2.068, 3.102, 4.137 g. $Ca_3(PO_4)_2$ in 1000 cc. none of which would show a precipitate, there were required, respectively, 9.5, 17.0, and 27.5 g. of gelatin. He found that gum arabic, blood serum, and starch may be used as protective colloids, but sugar and caramel do not give colloidal tri-calcium phosphate.

(c). Statement of the problem.

Since there is a possibility that a precipitate in col-
loidal form would not be so apt to hydrolyse, the purpose of
this research was first, to try to prepare colloidal tri-calcium
arsenate; second, if this colloid is obtained, to study its sta-
bility and ionization; and third, to study the stability and ion-
ization of other tertiary arsenates.

II.

Theoretical.

(a). Effect of colloidal dispersion on the tox-
icity of an insecticide.

Burton (3) found that the average diameter of the colloid-
al particles of gold, silver, and platinum range from 0.2 to 0.6
micron and other colloids are known to have particles that are
only one millimicron in diameter. These particles are therefore
much smaller than the particles of an ordinary precipitate which
is in suspension. Hence, since we have increased solution and
smaller particles, the toxicity of an insecticide should be in-
creased when it is in a colloidal form.

(b). Permanence of suspension.

When peptized, colloids remain suspended or disbursed for
an indefinite period of time. On the other hand certain sus-
pensions are often settled within a few hours.

(c). Protective effects against weathering.

If a colloidal solution of tri-calcium arsenate could be
used, it would not only have an increased toxicity, but it would
also tend to gelatinize on the foliage of the plant on which it

is sprayed. This gelatinous form would not be so easily washed off by the rain and would therefore materially reduce the number of sprayings necessary each year. It might be thought that this gelatinous coating would cover the pores of the leaves and in this way interfere with the respiration and transpiration of the leaves. However, sprays are not often applied so heavily but what the liquid collects in tiny droplets instead of forming a solid coating.

III.

Experimental.

(a). Preparation of the colloid.

A calculated amount of KOH solution was added to a solution of KH_2AsO_4 to form K_3AsO_4 solution. This solution was filtered and diluted to 3N. A solution of $CaCl_2$ was made up, filtered, and diluted to N.

Five cc. of the 3N potassium arsenate solution were diluted to 500 cc. and 15 cc. of the N. calcium chloride solution were diluted to 500 cc. Seventeen g. of gelatin were added to the calcium chloride solution and with both solutions near boiling, the arsenate solution was added slowly to the calcium chloride and gelatin solution. The stirring was continued for a few moments after the K_3AsO_4 solution had been added. This gave a solution or suspension which was white by reflected light and yellowish color by transmitted light. This solution gelatinized after standing about 20 hours. When diluted with two parts of water, it gave a clear, water white solution, which did not gelatinize and which remained clear for several days. An increased

amount of gelatin made a more viscous jelly. When the solutions were heated to about the melting point of gelatin (40° C.), instead of 100° C. the product appeared to be the same as was obtained in the other case. $Ca(NO_3)_2$ was tried in place of the $CaCl_2$ but the jelly did not seem to remain viscous quite as well.

An attempt was also made to make the colloidal $Ca_3(AsO_4)_2$ by dropping H_3AsO_4 into a paste of $Ca(OH)_2$ similar to the method recommended by Reedy and Haag (1). The gelatin was dissolved in the arsenic acid. This method proved unsuccessful because the gelatin seemed to slow the reaction too much. Even when the solution was made distinctly acid (phenolphthalein), by the time the upper part of the solution had gelatinized, the lower part would be decidedly colored, showing that the OH ions were again in excess. It was thought at first that this formation of OH ions indicated that hydrolysis was taking place but the fact that only a fraction of the calculated amount of arsenic acid was necessary to make the solution acid seems to show rather conclusively that it was the slowness of the reaction which caused the phenomena.

The above concentrations give a 0.015 N solution of Ca_3-$(AsO_4)_2$ or 0.995 g. of tri-calcium arsenate per liter.
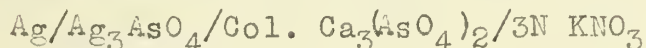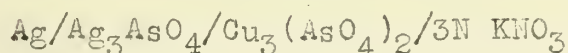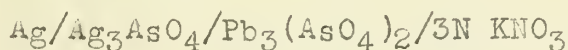
(b). Preparation of other arsenates.

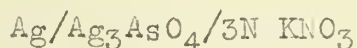Calculated amounts of the K_3AsO_4 solution were added to solutions of $AgNO_3$, $Pb(NO_3)_2$, and $Cu(NO_3)_2$ to form Ag_3AsO_4, $Pb_3(AsO_4)_2$, and $Cu_3(AsO_4)_2$ respectively. In each case the product was filtered, thoroughly washed, and then dried on a clay plate. Each product was kept in a stoppered sample bottle.

(c). Determination of the solubilities

of the arsenates.

The solubilities of the arsenates were determined by meas-
uring their electromotive forces, when used as half cells with
silver electrodes, and then calculating the ion concentrations
from the equation:

$$E = 0.0585 \log C'/C''$$

The half cells (used against N/10 Cal.) were:

$Ag/Ag_3AsO_4/3N\ KNO_3$

$Ag/Ag_3AsO_4/Pb_3(AsO_4)_2/3N\ KNO_3$

$Ag/Ag_3AsO_4/Cu_3(AsO_4)_2/3N\ KNO_3$

$Ag/Ag_3AsO_4/Col.\ Ca_3(AsO_4)_2/3N\ KNO_3$

The setup used was the ordinary one consisting of a stor-
age battery, potentiometer box, variable resistance, galvanom-
eter, and standard cell.

Considering E' as the potentiometer reading and using a
N/10 AgCl cell as a reference, the above equation becomes:

$$E' - .0474 = .0585 \log C(AgCl)/C(Ag_3AsO_4)$$

$$= .0585 \log(Ag^+)AgCl - .0585 \log (Ag^+)Ag_3AsO_4$$

The concentration of Ag ions in N/10 AgCl is 1.94×10^{-9}
and after substituting this value in the equation, it becomes:

$$E' - .0474 = .0585 \log 1.94 \times 10^{-9} - .0585 \log (Ag^+)Ag_3AsO_4$$

$$E' = .0474 + .0585 \log 1.94 \times 10^{-9} - .0585 \log (Ag^+)Ag_3AsO_4$$

Whitby (4) found that the solubility of Ag_3AsO_4 was
8.5×10^{-4} g. per 100 g. of solution. This is equal to 8.5×10^{-3} g. per liter of solution.

Changing this to moles it becomes:

$8.5 \times 10^{-3}/462.6 = 1.839 \times 10^{-5} = (As\bar{O}_4^-)$

$1.839 \times 10^{-3} \times 3 = 5.517 \times 10^{-5} = (Ag^+)$

Hence:

$$(Ag^+)^3 \times (As\bar{O}_4^-) = (5.517 \times 10^{-5})^3 \times (1.839 \times 10^{-5})$$
$$= 308 \times 10^{-20}$$

Therefore:

$$(Ag^+) = 308 \times 10^{-20}/ (As\bar{O}_4^-)$$

Substituting, the equation becomes:

$$E' = .0474 + .0585 \log 1.94 \times 10^{-9} - .0585 \times$$
$$\log 308 \times 10^{-20}/ (As\bar{O}_4^-)$$

$$E' = .0474 + .0585 \log 1.94 \times 10^{-9} - .0585 \times \log$$
$308 \times 10^{-20} + .0585 \log (As\bar{O}_4^-)$

Combining the terms which are constant for this work, the equation becomes:

$$E' = \text{constant} + .0585 \log (As\bar{O}_4^-)$$
$$= 0.67905 + 0.0585 \log (As\bar{O}_4^-)$$

$$\text{Log } (As\bar{O}_4^-) = \frac{(E' - 0.67905)}{0.0585}$$

The following readings were made:

No. 1. Silver arsenate (to try and check Whitby's results).

No. 2. Copper arsenate.

No. 3. Lead arsenate.

No. 4. A piece of gelatin from a Colloidal calcium arsenate solution several days old. (Made from $Ca(NO_3)_2$).

No. 5. Some colloidal calcium arsenate which had been made from calcium **nitrate**, but had been diluted with two parts of water and therefore had never gelatinized.

The above readings were taken after the cell had been made

up for at least 24 hours.

No. 6. Colloidal calcium arsenate made with $CaCl_2$. This reading was taken immediately after the gelatinous colloid had been put in the cell.

No. 7. No. 6 after standing for 72 hours.

No. 8. Same as No. 6 but made with $Ca(NO_3)_2$ instead of $CaCl_2$.

No. 9. No. 8 after standing for 72 hours.

Results.

Reading No.	Reading (Volts)	$(As\overline{\overline{O}}_4^{\overline{}})$
1.	0.1820	3.185×10^{-9}
2.	0.1828	3.295×10^{-9}
3.	0.1933	5.000×10^{-9}
4.	0.1155	2.330×10^{-10}
5.	0.1215	2.955×10^{-10}
6.	0.0716	4.100×10^{-11}
7.	0.0325	8.890×10^{-12}
8.	0.1566	1.172×10^{-9}
9.	0.1425	6.720×10^{-10}

IV.

Summary.

Calculating from the solubility given by Whitby (4), reading NO. 1 should give the concentration of the AsO_4 ions as 1.84×10^{-6} instead of 3.185×10^{-9}.

This difference makes the accuracy of the other figures rather doubtful. Even though the figures may not be quite accurate, however, they seem to show that the copper and lead ar-

senates are a little more soluble than the silver arsenate;
that colloidal calcium arsenate, especially when prepared with
$CaCl_2$, is even more insoluble than the silver arsenate; and that
none of these arsenates hydrolyses to any appreciable extent.

10.

V.

Bibliography.

(1). J. Ind. & Eng. Chem. $\underline{13}$, #11, p. 1038 (Nov. 1921).

(2). Koll. Zeit. $\underline{28}$, 145-8 (1921).

(3). Phil. Mag. $\underline{11}$, 425 (1906).

(4). Zeit. Anorg. Chem. $\underline{67}$,107.